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EPR probing with Mn^{2+} ions of ZnO nanostructures

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ZnO nanostructures doped with transition metal ions (TMI) are the focus of intensive research efforts due to the wide range of potential applications based on their unique combination of semiconducting, piezoelectric and pyroelectric properties. In the case of the Mn^{2+} doped ZnO nanostructures, in particular, the interest was triggered by the possibility to obtain room temperature ferromagnetic properties, as predicted by Dietl et al [1]. The synthesis of doped ZnO nanostructures for specific applications is not an easy task. An efficient tailoring of the material properties involves knowledge and control of both structural aspects (size, morphology, crystallinity), as well as impurity content and distribution in the nanostructures.

We report here the results of electron paramagnetic resonance (EPR) investigations on Mn^{2+} doped ZnO nanoparticles (NPS), synthesized by a variety of thermo–chemical procedures, and nanostructured thin films, deposited onto r-cut sapphire substrates by RF magnetron sputtering at room temperature. The EPR spectra of weakly perturbing paramagnetic transition metal ions, such as Mn^{2+} ions substituting the Zn^{2+} in the host lattice, are extremely sensitive to small changes in the nature and configuration of the neighbouring ligand atoms/ions. We were thus able to evidence the dominance of size induced lattice disorder in ZnO NPs, independent of the synthesis procedures, and to establish an empirical relationship between the disorder induced EPR line broadening and the average crystallite size, determined by X-ray diffraction [2].

This result was further used to probe by EPR the nanocrystallization of the disordered ZnO:Mn^{2+}, prepared by thermal decomposition of hydrozincite, submitted to isothermal annealing in air [2,3]. We found out that the ZnO NPs growth takes place at lower temperatures by a structural relaxation mechanism, consisting in the rearrangement of atoms at the interfaces, driven by the reduction of the surface induced strain. At higher temperatures the growth process is driven by the reduction of the total grain boundary energy.

The crystallization process in nanostructured ZnO films submitted to pulse annealing treatments was investigated by correlated EPR and high-resolution transmission electron microscopy [4]. Based on the observed correlation between the lattice disorder/crystallite size and the EPR line broadening we have determined the localization and dynamics of the Mn^{2+} impurities. Our results allow the fine-tuning of the synthesis conditions for both ZnO NPs and nanostructured films, aiming to obtain the required structural properties and impurity content and distribution.

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